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Electronic Structure of GaAs*

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Abstract

Using a non-local pseudopotential, including spin-orbit interactions, we have calculated a band structure for GaAs which is in excellent agreement with electroreflectance, wavelength modulation, and photoemission experimental results. An order of magnitude in accuracy has been gained over existing band structures; the largest discrepancy with Schottky barrier electroreflectance measurements is less than 0.08 eV. The conflicts presently existing in the interpretation of the E_0' reflectivity structure are resolved.

We have calculated what we believe to be the most accurate band structure for GaAs to date. In fact, due to the extensive experimental studies on this compound, this band structure may be the most accurate band structure, over a large energy range, available for any material. The largest discrepancy between the experimental critical point energies, as determined by the Schottky barrier electroreflectance of Aspnes and

Studna[1] and as calculated by our non-local pesudopotential scheme is less than 0.08 eV. Further, we are able to achieve comparable agreement with the derivative reflectivity spectrum from wavelength modulation measurements, and the electronic density of states as measured by photoemission experiments. This represents nearly an order of magnitude improvement over previous band structure calculations. We are also able to confirm the existence of the critical points of Δ symmetry appearing in the E_0' structure, which lie about 10% of the way from Γ to X, in agreement with the proposed assignment of Aspnes and Studna.[1] Spin-orbit interactions are found to be of prime importance in the formation of these critical points.

The band structure was calculated using the Empirical Pseudopotential Method (EPM) which has been discussed extensively elsewhere.[2] Since this method requires experimental information as input to fix the form factors, the recent experimental advances in electroreflectance techniques, in particular those developed by Aspnes,[1,3] and high resolution photoemission spectroscopy,[4] have proven to be quite valuable. According to Aspnes and Studna their electroreflectance measurements on GaAs have resulted in an order of magnitude improvement in the resolution and accuracy in the determination of critical point energies as compared to previous spectroscopic work.[1] In addition, the advent of high resolution photoemission spectroscopy has supplied us with detailed information on the lowest lying valence bands in semiconductors. This information, in turn, has indicated the necessity of non-local corrections to the usual

local pseudopotential calculations.[5,6] While these corrections are not significant over a limited energy range, for example, in obtaining an optical spectra where the top valence band and bottom conduction bands are of prime importance, they can be crucial in calculating a density of states where all the valence bands are required. It is these two experimental areas of advancement, then, which have made an extremely accurate band structure possible.

In our calculation we have taken an atomic pseudopotential of the form,

$$V_{NL}(\underset{\sim}{r}) = V_L(r) + A_2 \exp(-r^2/R^2)\,\mathcal{P}_2 \qquad (1)$$

where $V_L(r)$ is the usual local pseudopotential, and $\mathcal{P}_2$ projects out the $\ell = 2$ angular momentum component. This non-local pseudopotential is quite similar to the one used recently by us in Ge.[7]

The crystal potential is then taken to be a sum of these atomic pseudopotentials, and the local part can be expressed in terms of symmetric and antisymmetric pseudopotential form factors.[2] For this calculation the symmetric form factors were given by $V^S(3) = -0.214$, $V^S(8) = 0.014$, $V^S(11) = 0.067$ Ryd., and the antisymmetric form factors by $V^A(3) = 0.055$, $V^A(4) = 0.038$, $V^A(11) = 0.001$ Ryd. The non-local well depths were taken to be $A_2(\text{Ga}) = 0.25$ and $A_2(\text{As}) = 1.25$ Ryd. The parameter R in (1) is not of crucial importance in determining the band structure,[6] and since it is computationally simpler, we have constrained it to be equal to the radius used in Ge[7] for both the Ga and As contributions. Spin-orbit

interactions were included in our calculation in a method similar to the one used by Saravia and Brust in Ge.[8]

In Table I we compare our calculated critical point energies to the experimental results of Schottky barrier electroreflectance, wavelength modulation and photoemission. We also compare our results to two of the most accurate recent band calculations which have also included spin-orbit interactions. As can be noted a vast improvement over the previous calculations has been obtained. While the local EPM adequately gives the optical transitions, it yields significant errors when compared to the photoemission data. Here the OPW calculation results in better values, but it does not yield accurate optical transitions. Since a typical discrepancy between the local EPM or OPW theoretical results and the experimental values is on the order of 0.5 eV, and a typical non-local EPM error is on the order 0.05 eV, we have obtained an order of magnitude improvement.

Once the band structure has been obtained, the imaginary part of the dielectric function can be calculated, and by using the Kramers Kronig dispersion relations, a reflectivity obtained. In Figure 1 the experimental and theoretical modulated reflectivity is given for GaAs. And, as can be observed, the agreement is excellent.

By examining the energy gradients and dipole matrix elements throughout the Brillouin zone, it is possible to determine the origin of structure in the imaginary part of the dielectric function. In such a manner we have analyzed the contributions to the E_o' reflectivity structure.

This structure has been the subject of some discussion.[1,9] Rehn and Kyser using transverse electroreflectance observed only a Δ symmetry for this structure.[9] They attributed the structure to be derived from the pseudocrossing of the Δ_5 conduction bands. However, Aspnes and Studna have pointed out that this interpretation conflicts with band structure calculations where some Γ symmetry structure is predicted.[1] Further, they proposed that the Δ symmetry structure arises from a pair of M_1 critical points approximately 1/10th of the way from Γ to X. Our calculations agree with the Aspnes-Studna interpretation. We, indeed, find two M_1 critical points along Δ at between 5 to 10% of the way from Γ to X as indicated in Figure 2. It is these points along with contributions from Γ, which cause the structure at 4.5 eV (B) and 4.7 eV (C) in our derivative spectrum (Fig. 1). We have also found that by calculating the band structure with and without spin-orbit interactions, that these interactions are crucial in altering the band shape near Γ and producing the critical points.

Aspnes and Studna also noted the possibility of the pseudocrossing producing some very weak structure at 4.4 eV in the electroreflectance data.[1] This also agrees with our results. The dashed line in Fig. 2 indicates an M_o critical point position near the pseudocrossing. This M_o critical point produces the weak structure near 4.4 eV (A) in Fig. 1. It should be noted, however, that there exists a companion M_o critical point due to the spin-orbit splitting of the Δ_5 valence band. Since this companion occurs at about 0.1 eV higher energy, it is nearly degenerate with the E_o'

structure from Γ and Δ at 4.5 eV. In our calculated derivative spectrum it is masked by the stronger M_1 critical points, and this may also be the case in the electroreflectance measurements.

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We would like to thank Professor Y. R. Shen and Stanley Kohn for useful discussions and helpful comments. Part of this work was done under the auspices of the U.S. Atomic Energy Commission.

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Table Caption

Table I. Comparison of theoretical and experimental critical point energies for GaAs.

a) See Ref. 12

b) See Ref. 13

c) See Ref. 10

d) See Ref. 1

e) See Ref. 14

f) See Ref. 15

g) See Ref. 11

Figure Captions

Fig. 1. Comparison of theoretical (solid line) and experimental (dashed line) modulated reflectivity for GaAs. The experimental results are from Ref. 10. For A, B, C, see text.

Fig. 2. Calculated band structure for GaAs near Γ showing the critical point location for the E_0' structure. Also indicated (dashed line) is an M_0 critical point resulting from the pseudocrossing of the Δ_5 conduction bands.

Table I

Transition		Experiment: Reflectivity Structure	Experiment: Critical Point[d]	Theory: Non-local EPM	Theory: Local EPM[c]	Theory: OPW[g]
E_o	$\Gamma_8^v-\Gamma_6^c$	1.52[a]	1.52	1.51	1.52	1.34
$E_o+\Delta_o$	$\Gamma_7^v-\Gamma_6^c$	1.86[b]	1.86	1.86	1.87	1.66
E_1	$L_{4,5}^v-L_6^c$	3.02[c]	3.04	3.03	2.82	2.62
$E_1+\Delta_1$	$L_6^v-L_6^c$	3.25[c]	3.25	3.25	3.05	2.82
$E_o'(\Gamma)$	$\Gamma_8^v-\Gamma_7^c$	--	4.49	4.54	4.80	4.12
$E_o'+\Delta_o'$	$\Gamma_8^v-\Gamma_8^c$	--	4.66	4.71	4.93	4.30
$E_o'+\Delta_o+\Delta_o'$	$\Gamma_7^v-\Gamma_8^c$	--	5.01	5.05	5.28	4.62
$E_o'(\Delta)$	$\Delta_5^v-\Delta_5^c$	4.44[c]	4.53	4.54	4.38	--
$E_o'+\Delta_o'(\Delta)$	$\Delta_5^v-\Delta_5^c$	4.64[c]	4.71	4.70	4.55	--
	Σ	5.11[c]	5.14	5.07	4.88	--
	$X_7^v-X_6^c$	--	4.94	4.92	4.40	4.33
E_2	$X_6^v-X_6^c$	--	5.01	5.01	4.49	4.52
	$X_7^v-X_7^c$	5.64[c]	5.34	5.28	4.67	4.58
	$X_6^v-X_7^c$		5.42	5.38	4.76	4.67
		Photoemission: UPS[e]	Photoemission: XPS[f]			
$L_3^v-\Gamma_{15}^v$		0.8±0.2	1.4±0.3	1.31	0.85	1.06
$\Sigma_1^{min}-\Gamma_{15}^v$		4.1±0.2	4.4±0.2	4.23	3.35	--
$X_1^v-\Gamma_{15}^v$		6.9±0.2	7.1±0.2	6.88	6.23	6.43
$X_3^v-\Gamma_{15}^v$		10.0±0.2	10.7±0.3	9.87	10.00	10.24
$\Gamma_1^v-\Gamma_{15}^v$		12.9±0.5	13.8±0.4	12.55	12.10	12.44

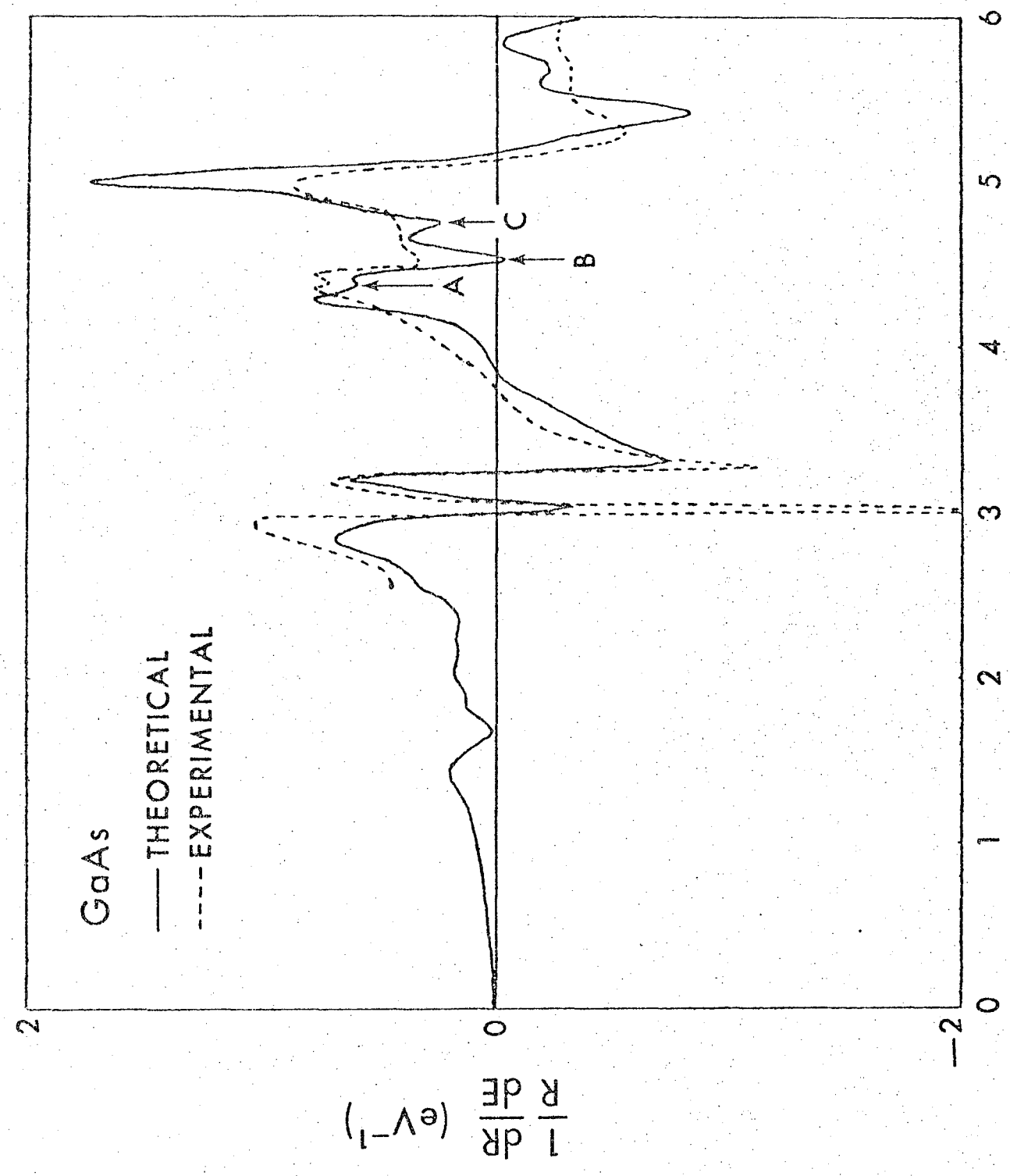
GaAs
THEORETICAL
EXPERIMENTAL
A
B
C
$\frac{1}{R}\frac{dR}{dE}$ (eV^{-1})
ENERGY (eV)
2
0
−2
0
1
2
3
4
5
6

Figure 1

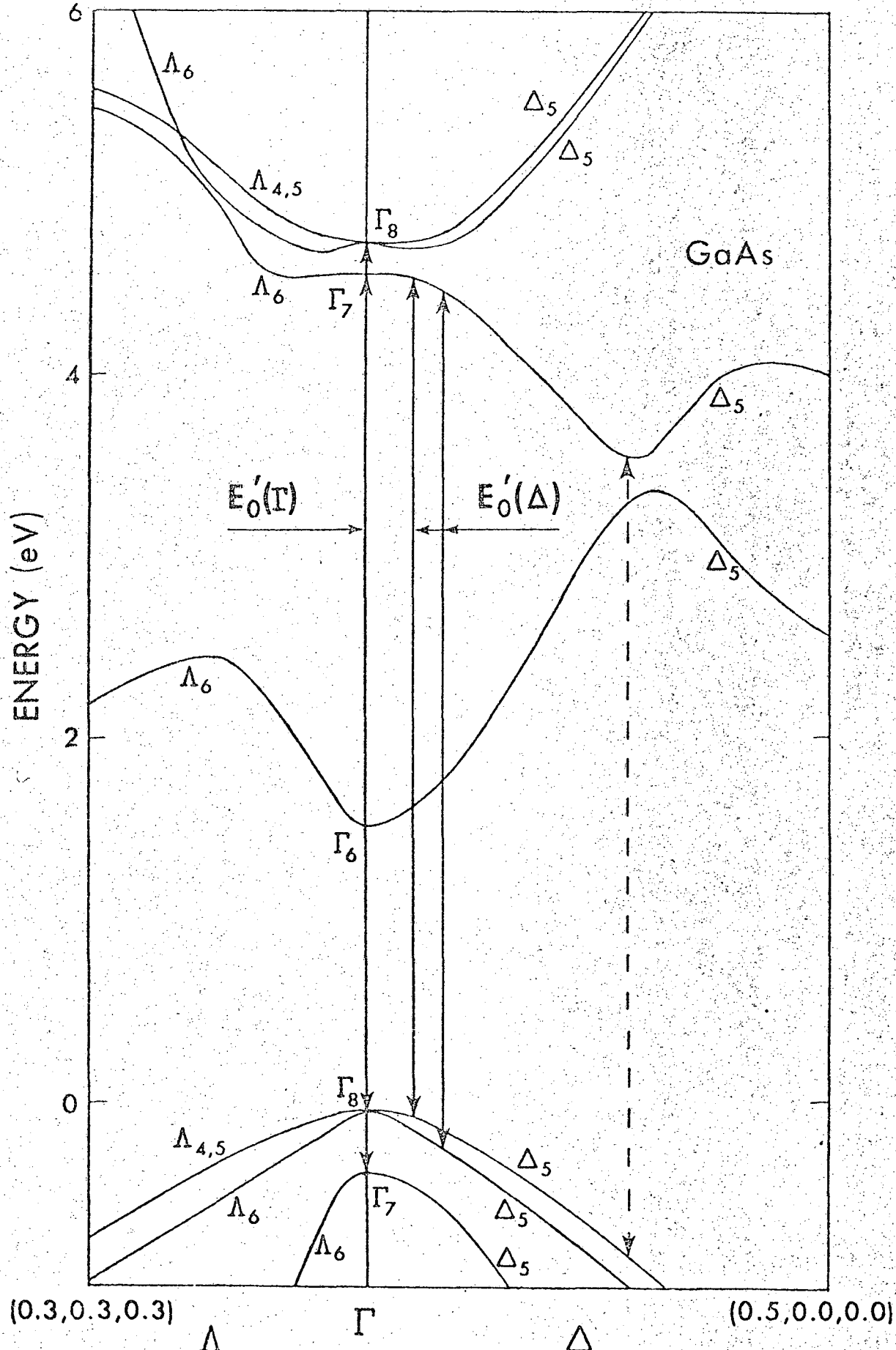
6
4
2
0
ENERGY (eV)
GaAs
Λ_6
Δ_5
Δ_5
$\Lambda_{4,5}$
Γ_8
Λ_6
Γ_7
Δ_5
$E_0'(\Gamma)$
$E_0'(\Delta)$
Δ_5
Λ_6
Γ_6
Γ_8
$\Lambda_{4,5}$
Δ_5
Λ_6
Γ_7
Δ_5
Λ_6
Δ_5
(0.3,0.3,0.3)
(0.5,0.0,0.0)
Λ
Γ
Δ

Figure 2

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